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Dated

16th August 1996





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GB9516057.8

By virtue of a direction given under Section 30 of the Patents Act 1977, the application is proceeding in the name of

FORBO-INTERNATIONAL S.A.,

Eglisau
Zurich
CH-819E
Switzerland

[ADP No. 07006323001]

Incorporated in Switzerland

2d, 2e and 2f: If there are further applicants please provide details on a separate sheet of paper.

☐ **Second applicant (if any)**

2d If you are applying as a corporate body please give:

Corporate name

Country (and State
of incorporation, if
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2e If you are applying as an individual or one of a partnership please give in full:

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3a Have you appointed an agent to deal with your application?

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please give details below

Agent's name

Cruikshank & Fairweather

Agent's address

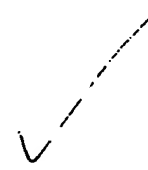
19 Royal Exchange Square
Glasgow

Postcode

G1 3AE

Agent's ADP
number

547002



3b: If you have appointed an agent, all correspondence concerning your application will be sent to the agent's United Kingdom address.

3b If you have not appointed an agent please give a name and address in the United Kingdom to which all correspondence will be sent:

Name

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- 4 AUG 1995

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FAT 1 77 UC

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Your reference

JTS/CN/LO/P06811GB

9516057.8

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Request for grant of a Patent Form 1/77

Patents Act 1977

1 Title of invention

- 1 Please give the title of the invention
- Polymer Product Manufacture

2 Applicant's details

☐ First or only applicant

- 2a If you are applying as a corporate body please give:

Corporate name

Forbo-Nairn Limited

Country (and State of incorporation, if appropriate)

England UK

- 2b If you are applying as an individual or one of a partnership please give in full:

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Forenames

- 2c In all cases, please give the following details:

Address

Bassington Avenue
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NE23 8AD

Country

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06613046002 R.

- 7 The answer must be marked if:
- any applicant is not an inventor
 - there is an inventor who is not an applicant, or
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8 Please supply duplicates of claim(s), abstract, description and drawing(s).

Please mark correct box(es)

- 9 You or your appointed agent (see Rule 90 of the Patents Rules 1990) must sign this request.

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7 Inventorship

7 Are you (the applicant or applicants) the sole inventor or the joint inventors?

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Yes ☐

No ☒

A Statement of Inventorship on Patents Form 7/77 will need to be filed (see Rule 15).

8 Checklist

8a Please fill in the number of sheets for each of the following types of document contained in this application.

Continuation sheets for this Patents Form 1/77

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Claim(s)

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Description

9

Abstract

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Drawing(s)

—

8b Which of the following documents also accompanies the application?

Priority documents (please state how many)

--

Translation(s) of Priority documents (please state how many)

--

Patents Form 7/77 – Statement of Inventorship and Right to Grant
(please state how many)

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Patents Form 9/77 – Preliminary Examination/Search

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Patents Form 10/77 – Request for Substantive Examination

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9 Request

I/We request the grant of a patent on the basis of this application.

Caroline A. Farwell

Signed

Date 03. 08. 1995
(day month year)

(Agents)

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① Reference number

4 Agent's or
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number (if applicable)

JTS/CN/LO/P06811GB

⑤ Claiming an earlier application date

5 Are you claiming that this application be treated as having been filed on the date of filing of an earlier application? _____

Yes ☐ No ☒ \Rightarrow go to 6



please give details below

☐ number of earlier application or patent number

 filing date

day	month	year
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☐ and the Section of the Patents Act 1977 under which you are claiming:

15(4) (Divisional) ☐ 8(3) ☐ 12(6) ☐ 37(4) ☐

⑥ Declaration of priority

6 If you are declaring priority from previous application(s), please give:

Country of filing

Priority application number
(if known)

Filing date
(day, month, year)

① If you are declaring priority from a PCT Application please enter 'PCT' as the country and enter the country code (for example, GB) as part of the application number.

Please give the date in all number format, for example, 31/05/90 for 31 May 1990.

POLYMER PRODUCT MANUFACTURE

The present invention relates to the manufacture of polymer products.

Many plastics products are manufactured by forming a feed
5 stock of polymer material into a desired shape or
configuration using well known processes such as for
example, extrusion, spread sheet formation or hot roll
calendering in the case of plastics sheet manufacture.
Especially in the case of spread sheet formation, this
10 requires the polymer material to be substantially fluid. At
the same time though it is often necessary to limit the
temperature of the polymer material in order to avoid
degradation thereof or impairment of its physical
properties.

15 In the case of polyvinyl chloride (PVC) and like polymers
there is more or less widely used the so-called vinyl
plastisol technology in which small particles of PVC powder
are suspended in a liquid carrier in order to reduce the
viscosity thereof to a sufficient level to allow the
20 physical manipulation thereof whether by spread coating or
hot roll calendering or a similar process, to proceed under
practical conditions, and upon subsequent heating of the
mixture the PVC crystals melt into an amorphous mass into
which the liquid carrier is absorbed. This technology is
25 however peculiar to vinyl polymers and cannot be extended to
other polymers.

In practice though significant environmental problems can
arise caused by the migration of liquid plasticizers out of
the material. The final product may also suffer loss of
30 performance due to the presence of residual liquid
plasticiser and/or due to leaching thereof from the product
over an extended period of time in use thereof.

In the case of polyolefins it has been previously proposed
to include small amounts of oils and the like to fine tune
35 their processability. It has also been proposed to

manufacture polyolefin products containing more or less large amounts of oils in order to modify processability and produce particular product characteristics such as softness. The utility of such products is however substantially
5 restricted since they contain relatively large amounts of liquid. It has not previously been possible though significantly to extend the processability of polyolefins without substantially compromising the physical properties of the final product.

10 It is an object of the present invention to avoid or minimize one or more of the above disadvantages.

It has now been found that the processability of polyolefins in the manufacture of products from polyolefins can be substantially improved and extended by inclusion of a
15 plasticiser or processing aid comprising a selectively polymerisable liquid monomer system which is substantially non-polymerisable under the product forming, e.g. extrusion, spread-coating or calendering, conditions used in the product sheet material manufacturing process whilst being
20 substantially polymerisable subsequently so as to produce a product substantially free of liquid plasticiser. In this connection it will be understood that there is normally used an initiator substance in order to induce polymerisation of the monomer and which is included together with the monomer
25 in the monomer system. Accordingly in such cases it is important that the initiator is one that is selectively activatable i.e. is substantially inactive under the polyolefin product forming conditions but may subsequently be activated under suitable plasticiser monomer
30 polymerisation or curing conditions.

Thus in one aspect the present invention provides a process for the manufacture of a plastics product from a polyolefin resin comprising the steps of:
providing a plasticiser monomer system which is
35 substantially non-polymerisable under the product sheet forming, e.g. extrusion, spread-coating or calendering,

conditions used in the product sheet material manufacturing process, whilst being substantially polymerisable subsequently so as to produce a product substantially free of liquid plasticiser;

- 5 bringing said plasticiser monomer into intimate admixture with said polyolefin resin (and any additives that may be used therewith);
forming said mixture into a desired product form; and subsequently inducing polymerisation of said plasticiser
10 monomer so as to provide a final product substantially free of liquid plasticiser.

The invention also extends to plastics products when manufactured by the process of the present invention.

- With the process of the invention the processability of the
15 polyolefin in the manufacture of various product forms from the polyolefin is substantially improved thereby extending the range of possible products which can be made from the polyolefins, and allowing significant economic benefits e.g. in relation to increasing use of equipment previously only
20 usable for other polymer systems, reduced energy requirements, less demanding product forming conditions etc. Also design flexibility in relation to the particular form of the polyolefin in the final product may be significantly enhanced.

- 25 Thus the present invention provides advantages in both processing and in the properties of the resulting materials, and opens up polyolefins to a range of processing options that are similar to those used in the vinyl plastisol area and from which polyolefins were previously excluded. The
30 incorporation of different amounts of different types of monomers with a wide range of crosslinking densities can moreover provide a broad range of physical and chemical properties in the final product. Combined with the ability of this system to contain large amounts of fillers and other
35 additives, materials can be prepared that range from soft elastomers to tough plastics, from clear to opaque, from

coatings on fabrics to structural materials. The versatility of olefin based systems is thus greatly enhanced and extended.

One example of this idea is the formation of a multi-layer floor covering from metallocene polyolefins and a "liquid paraffin like" monomer system using spread coating technology. Such a material is disclosed in our copending International patent application of even date.

The range of polyolefins that can be used in accordance with the present invention include: polyolefin polymers, copolymers, and terpolymers prepared by any known polymerization technique - such as free radical, Ziegler-Natta, single-site catalysed (metallocene) etc. Moreover with such polymers all of the possible polymer geometries can be utilized - such as straight chain, branched, stereoregular, etc. The hydrocarbon polymer chains may also be substituted in known manner e.g. by incorporation of functional monomers or by post-polymerization functionalization. Copolymers of olefins and acidic monomers (such as Surllyn from Dupont) or polar monomers (such as Enathene, an ethylene/butyl acrylate copolymer from Quantum Chemical) would be examples of such materials. Polymers prepared by extruder reaction grafting of monomers, such as maleic anhydride, to non-functional polyolefins would also be examples of this.

A variety of polymeric and non polymeric additives can be incorporated into these polyolefin systems. This includes the full range of inorganic fillers and reinforcements, fire retardants, stabilizers, dyes and pigments, and the like. The polymeric additives would include impact modifiers, processing aids, compatibilizers, blending aids, as well as polymeric stabilizers, flame retardants, pigments, and texturing aids. Gas inclusions, in the form of either open or close cell foam can also be part of the polyolefin system. This can be achieved both through the use of a chemical blowing agent or through the mechanical

incorporation of air, or another gas, into the system.

The plasticiser monomers that can be used in accordance with the present invention are those that are solvents for the main polymer component(s) of the polyolefin product. They need not, and would normally not, be solvents for the inorganic components nor for other components, which may themselves also be polymers, such as impact modifiers, texturing aids, pigments, and some compatibilizers. The monomers will, in general, have a long segment that is "polyolefin like" with an end group that is capable of free radical polymerization. Typical "polyolefin like" structures are hydrocarbons with ten or more carbon atoms, and examples of such groups would be lauryl ($C_{12}H_{25}$) and stearyl ($C_{18}H_{37}$). Such structures can be linear, branched, or cyclic; depending in part upon the structure of the polyolefin. The terminal polymerizable group can be a simple unsubstituted double bond, such as in 1-dodecene or a more complex unit such as a methacrylate, as in stearyl methacrylate.

Along with the plasticiser monomer or monomers, compounds that generate free radicals at elevated temperatures and optionally crosslinking monomers may be used to cure the resulting products and to provide enhanced properties. Many classes of free radical generators can be used, but materials in the peroxide, ketone peroxide, peroxydicarbonate, peroxyester, hydroperoxide, and peroxyketal families are of particular use. Also of utility are several classes of azo compounds and a variety of photoinitiators. The characteristics needed in these compounds is that they are substantially non-polymerisable i.e. remain essentially dormant during the initial mixing, compounding, and product fabrication process but can be induced to produce free radicals at a rate that will initiate a polymerization of the monomer e.g. when the temperature is increased, or when exposed to the appropriate radiation. For example a material such as t-butyl perbenzoate has a half life of over 1000 hours at 100 C,

while having a half life of less than 2 minutes at 160 C. In a polymer/monomer system containing such an initiator would be possible to process the system into the finished product form (i.e. shape or configuration) at 100 C and then
5 cure the system by a brief exposure at 160 C.

When polyfunctional monomers are included in the system then a continuous crosslinked polymer system can be formed from the monomer. Optionally additional radical generators can be included that will provide cross linking of the pre
10 existing polyolefin system. A Semi-IPN (inter-penetrating network) is obtained when one of the co-continuous systems (i.e. the pre-existing polyolefin and the polymerised plasticiser monomer) is crosslinked. When both systems are crosslinked an IPN is formed.

15 To prevent premature polymerization of the plasticiser monomer it may be useful to add additional inhibitors to the system. Most commercial monomers are provided with inhibitors to prevent polymerization during handling and processing. The level of such inhibitors should be
20 increased to compensate for the time spent under the polyolefin polymer product forming conditions, i.e. the conditions used to form the base polyolefin polymer into a sheet or some other shape or configuration. In this connection the temperature is usually the most significant
25 factor, but other conditions may also be relevant. Thus for example stearyl methacrylate is commercially provided with 275 parts per million (ppm) of the monomethyl ether of hydroquinone (MEHQ). Depending on the times and temperature involved 1000 ppm MEHQ, or more, may be needed. Inhibitors
30 from a wide range of chemical families made be used for this purpose.

The polymeric system and the monomeric system can be combined in a variety of ways to give a low viscosity plasticised material that can be used to manufacture many
35 types of products using several different fabrication techniques. The combination of the solid and liquid

components can be done in any suitable manner e.g. by using a continuous or batch mixer, various types of continuous and batch blending devices, and various types of extruders. In all these types of equipment the solid components are mixed together at sufficient temperature and with sufficient shear to achieve both distributive and dispersive mixing. The liquid is introduced at the needed temperature and shear to dissolve the principal polymeric components and to obtain good distributive mixing and dispersive mixing of the insoluble components with the resulting fluid. The fluid system is then held at a temperature that retains the required fluidity for the fabrication of the final product form. In general this will ususally be in the range from 80 to 120°C.

15 The fabrication techniques that can be used for the fabrication of the final product form include: spread coating, molding, cast molding, strand coating, spray coating, cellular coating, and cellular molding. The types of products that can be prepared by spread coating include: upholstery material, automotive roofing, apparel fabrics, wall coverings, floor covering, carpet backing, paper coating, and roll coating. Rotational molding can be employed to make such items as storage tanks, luggage shells, syringe bulbs, and inflatable toys. Dip coating can be used to produce gloves, wire racks, tool handles, and electric parts. Strand coating can be used to cover wire for such uses as insect screens; spray coating can be used to provide protective coatings on appliances and furniture; cellular coating can provide foam systems for fabrics, carpet backing, and upholstery; and foam molding can be useful for making bumpers, padding, flotation devices, and insulation.

Further preferred features and advantages of the invention will appear from the following detailed Example given by way of illustration.

Example 1 - Preparation of Multi-Layer Floor Covering Using Multiple Spreading

A floor covering material is prepared as a four layer structure by a multiple spreading application technique. At an initial station a glass fibre web is saturated with polymer having composition A at a temperature of approximately 100°C. At a separate station a back coating of composition B is applied to the bottom side of the polymer saturated glass web at approximately 100°C. At another separate station the foamable layer, composition C, is applied to the top side of the polymer saturated glass web at approximately 100°C. A decorative pattern is then printed upon the foamable layer using a continuous printing process that employs, in one of several inks, benzotriazole, to deactivate the accelerated foaming system thereby to produce a chemical debossing effect upon foaming. In a further separate coating step of the process a clear wear layer of composition D is applied to the foamable layer at approximately 100°C. The structure is then passed through an oven system to crosslink the layers at approximately 170°C and then expand the foam layer to approximately 200°C. The final cured, decorated and embossed product constitutes the floor covering material.

A. (<u>Saturant Layer</u>)		<u>PHR</u>
25	Exact 4038 MPO Resin	100
	Calcium Hydroxide	66.7
	Stearyl Methacrylate (settable plasticizer)	90
	Trimethylolpropane trimethacrylate (settable plasticizer)	10
30	Lupersol 230 (free radical polymerisation initiator from Atochem)	5
	Irganox 1010	0.1
	DSTDP	0.1
	Ultranox 626	0.05
35 B. (<u>Backcoat Layer</u>)		<u>PHR</u>
	Exact 4038	100

	Calcium Carbonate	300
	Stearyl Methacrylate	90
	Trimethylolpropane trimethacrylate	10
	Lupersol 230	5
5	Irganox 1010	0.1
	DSTDP	0.1
	Ultranox 626	0.05
C. (<u>Foamable Layer</u>)		
	Exact 5008	<u>PHR</u>
		100
10	Calcium Carbonate	66.7
	Stearyl Methacrylate	90
	Trimethylolpropane trimethacrylate	10
	Lupersol 230	5
	Celogen OT (chemical Blowing agent	
15	from Uniroyal)	4
	Zinc Oxide	2
	Luchem HA -B18	0.15
	Irganox 1010	0.1
	DSTDP	0.1
20	Ultranox 626	0.05
D. (<u>Wear Layer</u>)		
	Exact 3017	<u>PHR</u>
		100
	Stearyl Methacrylate	70
	Trimethylolpropane trimethacrylate	30
25	Lupersol 230	5
	Vinyl trimethosilane	4
	Luchem HA -B18	0.3
	Irganox 1010	0.1
	DSTDP	0.1
30	Ultranox 626	0.05